

Convenient Preparation and Vibrational Spectra of Cyclodecasulfur, S₁₀, and of the Adduct S₆ · S₁₀ [1]

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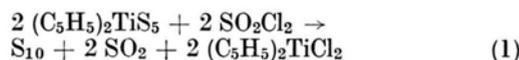
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Cyclodecasulfur, Preparation,
Vibrational Spectra, Cycloheptasulfur Oxide,
Cyclohexasulfur Dioxide

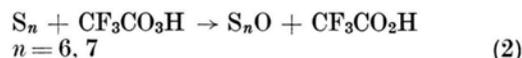
Thermal decomposition of S₆O₂ and S₇O, respectively, in CH₂Cl₂ or CS₂ solution at temperatures between 20 and 5 °C yields SO₂, polymeric sulfur and S₁₀ which was obtained as pure single crystals in yields of 7–11% with regard to the starting materials S₆ and S₇, respectively. Infrared and Raman spectra of S₁₀ as well as of the new molecular addition compound S₆ · S₁₀ are reported.

S₁₀ is one of the thermodynamically instable allotropes of sulfur and originally was prepared according to:

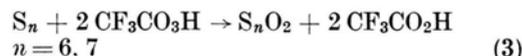


S₁₀ was obtained as instable, intensely yellow, light-sensitive crystals [2] which have recently been shown [3] to consist of cyclic molecules of D₂ symmetry with bond distances ranging from 203.3 to 207.8 pm. We now report two more convenient syntheses for S₁₀ starting from S₆ and S₇, respectively, as well as the vibrational spectra of S₁₀ for the first time.

When S₆ and S₇ in CH₂Cl₂ solution are oxidized by trifluoroperoxyacetic acid at –20 °C, S₆O [4] and S₇O [5], respectively, are formed:



Oxidation by an excess of peroxyacid results in the formation of S₇O₂ [1] and presumably S₆O₂ [6] whose structures are still unknown:

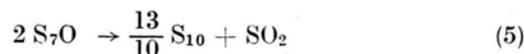


All these oxides form instable orange-yellow crystalline solids which decompose to SO₂ and insoluble polymeric sulfur at 25 °C. However, when S₆O₂ or S₇O are stored as CS₂ or CH₂Cl₂ solutions for several days at temperatures between 20 and

Table I. Raman and infrared spectra of solid S₆, S₁₀, and S₆ · S₁₀ (in cm⁻¹; Raman intensities in brackets, spectrometer Cary 82, spectral bandwidth 1.3–1.5 cm⁻¹, krypton laser 647.1 nm, sample temperature –90 ± 10 °C; IR spectrometer PE 325, CsI discs at 25 °C, intensities: vs very strong, s strong, m medium, w weak, vw very weak, sh shoulder).

S ₆	Raman		IR		
	S ₁₀	S ₆ · S ₁₀	S ₆ (ref. [10])	S ₁₀	S ₆ · S ₁₀
	495(6)				
	487(16)	489(4)		482 w	483 w
	481 sh	479(69)			
471(100)	469(36)	466(38)	463 s	456 vw	461 vs
461(2)	466 sh	461 sh			
		455 sh			
451(44)		451(21)			
	425(18)	428(19)			
	403(2)	408(4)			
			390 vw		387 vw
			313 s		315 sh
					310 m
		272(31)			
266(55)	255(5)	265(3)			264 vw
		249(6)			
	243(24)	240(15)		244 sh	242 vs
				239 vs	240 sh
	231(3)	228(3)		226 sh	231 sh
		225(1)		220 s	221 m
		207(17)			211 s
203(86)		201(19)		204 m-s	207 sh
					201 sh
	178(31)	172(29)	180 s		
	145(2)	155(3)			
	131(20)	136(10)			
106(3)	100(19)	103(26)			
		92(17)			
84(46)	85(33)	81(31)			
	73(100)	76(23)			
		64 sh			
	51(6)	58(92)			
	39(37)	42(100)			
	29(26)	34(34)			

5 °C they decompose to SO₂, polymeric sulfur, and S₁₀ which due to its low solubility crystallizes from the solutions as tetragonal crystals whose vibrational spectra (Table I) are very similar to those of S₁₀ obtained from (C₅H₅)₂TiS₅ and SO₂Cl₂. One of these crystals has been used for the X-ray structural analysis of S₁₀ [3].



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Since S_6O_2 and S_7O are prepared in CH_2Cl_2 solutions it is not necessary to isolate these compounds but mixtures of S_n ($n = 6, 7$) and CF_3CO_3H in CH_2Cl_2 are simply stored for several days at low temperatures till S_{10} has been formed. The over-all yields of S_{10} according to equations (2) to (5) amount to 11% in the case of S_6 and to 7% in the case of S_7 as starting materials. Since both S_6 and S_7 can be easily obtained from S_8 [7, 8] the cyclic sulfur oxides now provide a method to indirectly prepare S_{10} from S_8 .

The reaction mechanism of the S_{10} formation is unknown, but presumably S_{10} is formed from the intermediate chain-like sulfur which results from the decomposition of S_6O_2 and S_7O , respectively, by ring opening and bimolecular SO_2 formation.

The vibrational spectra of S_{10} (Table I) are highly characteristic and can be used to detect S_{10} in mixtures with other sulfur allotropes. According to the molecular D_2 symmetry all 24 fundamental vibrations ($7a$, $6b_1$, $5b_2$, $6b_3$) are allowed in the Raman spectrum and all but the $7a$ vibrations are active in the IR spectrum. From the experiences with other sulfur rings [9] the stretching frequencies are expected in the 390 – 500 cm^{-1} region, the bending frequencies at 100 – 320 cm^{-1} and the torsional modes together with lattice vibrations in the 40 – 100 cm^{-1} region. The spectra given in Table I are in agreement with these expectations. A complete normal-coordinate analysis will be published elsewhere.

When S_{10} was prepared from S_6 according to several slightly different procedures the formation of a new sulfur allotrope was observed several times. This compound forms orange-yellow opaque crystals of melting point $92\text{ }^\circ\text{C}$ which can be stored at $25\text{ }^\circ\text{C}$ in the dark for several days without decomposition. The relative molecular mass was determined osmotically in CS_2 solution at $25\text{ }^\circ\text{C}$ as to 258 which corresponds to 8.0 sulfur atoms per molecule, but the vibrational spectra show that an isomer of S_8 can be excluded. The new compound was identified as a stoichiometric molecular addition compound of formula $S_6 \cdot S_{10}$ which can also be prepared in low yield from S_6 and S_{10} .

The vibrational spectra of solid $S_6 \cdot S_{10}$ are similar but not identical to superimpositions of the corresponding spectra of S_6 and S_{10} (Table I) indicating that the known D_{3d} and D_2 conformations of S_6 and S_{10} , respectively, are approximately preserved in $S_6 \cdot S_{10}$. The splitting of the e_g mode of S_6 at 203 cm^{-1} into a doublet in $S_6 \cdot S_{10}$ shows a nondegenerate site symmetry of the S_6 molecules and proves that $S_6 \cdot S_{10}$ is not a mixture of S_6 and S_{10} . Nor is it a solid solution since the relative intensities of the Raman lines arising from the S_6 and S_{10} constituents of $S_6 \cdot S_{10}$ were always the same with different samples proving a constant composition. However, in CS_2 solution at $0\text{ }^\circ\text{C}$ the adduct exhibits the Raman lines of S_6 and S_{10} only and, therefore, must be almost completely dissociated in agreement with

the measured average molecular size of 8 atoms. To our knowledge $S_6 \cdot S_{10}$ is the first example of an allotrope of a chemical element consisting of molecules of two different sizes.

Experimental

S_{10} from S_7 : The CF_3CO_3H solution was prepared from 1.23 ml H_2O_2 (80%) and 8.1 ml $(CF_3CO)_2O$ in 91 ml pure CH_2Cl_2 at $0\text{ }^\circ\text{C}$ according to the published procedure [4, 5]. Within 15 min 10.1 ml of the CF_3CO_3H solution were added dropwise at $0\text{ }^\circ\text{C}$ to a solution of 0.89 g S_7 in 100 ml pure CH_2Cl_2 . After stirring for 1 h the solution was kept at $20\text{ }^\circ\text{C}$ for 3 h. Subsequently the solvents were removed in a vacuum and the yellow residue was extracted with 5 ml CS_2 . After filtration 10 ml *n*-hexane were added to the CS_2 solution and the mixture was cooled to $-78\text{ }^\circ\text{C}$ for 15 h. The solid precipitate consisting of S_7 and S_{10} was isolated on a glassfrit D3, washed with ether, and dissolved in 3 ml CS_2 . After addition of 7 ml *n*-hexane the solution was cooled to $-20\text{ }^\circ\text{C}$ which resulted in the precipitation of 62 mg of pure S_{10} .

S_{10} from S_6 : The CF_3CO_3H solution was prepared from 4.7 ml H_2O_2 (80%) and 31 ml $(CF_3CO)_2O$ in 114 ml pure CH_2Cl_2 at $0\text{ }^\circ\text{C}$ [4, 5]. Within 20 min 100 ml of the CF_3CO_3H solution were added in the dark to 10 g S_6 dissolved in 1.9 l pure CH_2Cl_2 at $0\text{ }^\circ\text{C}$. After stirring for 90 min at $0\text{ }^\circ\text{C}$ the reaction mixture was stored at $5\text{ }^\circ\text{C}$ for 48 h and finally cooled to $-50\text{ }^\circ\text{C}$ which resulted in the crystallization of S_{10} from the turbid solution. The crystals were separated from the suspended polymeric sulfur by decantation and filtration (glassfrit D2) and washed with cold CH_2Cl_2 . Yield: 0.91 g S_{10} . Recrystallization from 1.8 l CH_2Cl_2 by dissolution at $25\text{ }^\circ\text{C}$ and crystallization at $-50\text{ }^\circ\text{C}$ yielded 0.68 g pure S_{10} as lemon-yellow tetragonal crystals which melt in the temperature range 80 – $105\text{ }^\circ\text{C}$ with decomposition and which are stable at $25\text{ }^\circ\text{C}$ in the dark for several days. After longer periods of time (10 days) polymeric sulfur is formed.

$S_6 \cdot S_{10}$ from S_6 : The CF_3CO_3H solution was prepared as above (S_{10} from S_6). Within 30 min 100 ml of the CF_3CO_3H solution were added in the dark to 10.0 g S_6 dissolved in 250 ml pure CS_2 at $0\text{ }^\circ\text{C}$. After stirring for 1 h the lower phase of the heterogeneous mixture was separated and discarded while the orange CS_2 phase was filtered and stored for 24 h at $5\text{ }^\circ\text{C}$. Cooling of the solution to $-20\text{ }^\circ\text{C}$ for 12 h resulted in the crystallization of colorless CF_3CO_3H from the turbid mixture which after filtration was mixed with 60 ml *n*-pentane of $-20\text{ }^\circ\text{C}$ and then cooled to $-78\text{ }^\circ\text{C}$. After 24 h 2 g of a mixture of S_6 and $S_6 \cdot S_{10}$ had been precipitated and were isolated by filtration on a glassfrit D2 and washed with *n*-pentane. This mixture was dissolved in 100 ml CS_2 at $25\text{ }^\circ\text{C}$ and little *n*-pentane was added til the solution had just become slightly

turbid. Cooling to $-20\text{ }^{\circ}\text{C}$, then to $-50\text{ }^{\circ}\text{C}$, and finally to $-78\text{ }^{\circ}\text{C}$ resulted in the crystallization of three fractions of $\text{S}_6/\text{S}_6 \cdot \text{S}_{10}$ mixtures of which only the first and the last one were rich in S_6 while the

middle fraction could be used to prepare pure $\text{S}_6 \cdot \text{S}_{10}$ by dissolution in 50 ml CS_2 at $25\text{ }^{\circ}\text{C}$ and cooling to $-78\text{ }^{\circ}\text{C}$. Yield: 0.72 g. The adduct is soluble in CS_2 and in CHBr_3 but not in *n*-pentane.

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- [1] Part 58 of the series "Sulfur Compounds"; this work was supported by the Deutsche Forschungsgemeinschaft and by the Technische Universität Berlin (FPS 5/4). Part 57, see R. Steudel, T. Sandow, *Angew. Chem.* in press.
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